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QUANTITATIVE DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY USING THE SELECTED ION MONITORING MODE

This document presents the procedures used in the performance of the above analytical procedures.

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1.0 PURPOSE

This document provides the procedures used by the staff of the Geochemical and Environmental Research Group (GERG) of the College of Geosciences at Texas A&M University for the quantitative determination of polynuclear aromatic hydrocarbons (PAH) in sample extracts using gas chromatography/mass spectrometry (GC-MS).

1.1 Applicability

The instrumental procedures described in this document are applicable to the quantitative analysis of extracts obtained from water, sediment, soil, tissue, and other sample matrices after appropriate extraction and purification.

1.2 Target Analyte List

The PAHs target compounds determined by this method and the surrogate used for quantitation (reference surrogate) are listed in Table 1.

1.3 Method Detection Levels

The analytical method detection limit (MDL) is determined on an annual basis following procedures outlined in Federal Register (1984), Vol. 49, No. 209: 198-199. MDLs for the multi-analyte groups are estimated as twice the MDL of the parent compound.

2.0 SAFETY

The hazards, toxicity or carcinogenicity of each compound or reagent used in GERG's standard operating procedures have not been precisely determined. However, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level. The laboratory maintains Material Safety Data Sheets (MSDS) which contain information regarding the safe handling of chemicals used at GERG's facilities. A reference file of MSDS is

available to all personnel involved with these materials. All laboratory personnel should direct any questions regarding safety issues to their supervisors or the Safety Officer.

3.0 QUALITY CONTROL

The quality control requirements for quantitative analysis are summarized in Table 2 with details provided in the following sections.

3.1 Mass Spectrometer Performance

3.1.1 The mass spectrometer performance is checked daily using PFTBA according to manufacturer's tuning procedures. These procedures include the checking of peak widths, mass axis calibration, and relative abundances of masses 69, 219, and 502 against manufacturer's recommended criteria. Isotope abundances are also checked according to the manufacturer's criteria.

3.1.2 Total cycle time (dwell times plus switching times) for all ions within a single descriptor must be one second or less.

3.2 Analyte Identification Criteria for Single Analyte Compounds

3.2.1 Retention Times

3.2.1.1 Qualitative identification of target compounds is based on a comparison of the retention times with the target compounds in the calibration curve with the retention time of target compounds found in the sample extract. The retention time of the compound in the extract should be within ± 4 seconds of the average retention time of the authentic compounds in the calibration standard.

3.2.1.2 The ion current responses for ions used for quantitation and confirmation purposes must simultaneously reach their maxima (± 2 seconds).

3.2.1.3 The ion current responses for the quantitation and confirmation ions used for the labeled standards must reach maximum simultaneously (± 2 seconds).

3.2.2 Qualitative Identification

The extracted ion current profiles of the quantitation ion (primary m/z) and the confirmation ion (secondary ion) for each target compound must meet the following QC acceptance criteria

3.2.2.1 The characteristic masses of each target compound must maximize in the same scan or within one scan of each other.

3.2.2.2 The retention time of target compounds in the sample must fall within ± 4 seconds of the retention time for the authentic compound in the calibration standards.

3.2.2.3 The relative peak heights of the primary ion compared to the confirmation (or secondary) ion mass for a target compound should fall within ±30 percent of the relative intensities of these masses in a mass spectrum (Table 3) obtained from a reference standard of that target compound.

3.2.2.4 A compound that does not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by the mass spectroscopist.

3.2.2.5 Supportive data includes the presence of the secondary ion having a ratio greater than ±30 percent of the primary ion which may be caused by an interference with the secondary ion.

3.2.2.6 The data not meeting these criteria are reported but appropriately qualified.

3.3 Analyte Identification Criteria for Multiple Analyte Groups

3.3.1 Retention Time Windows

Prior to all analytical sequences, a reference oil solution (GERG Standard Check) is analyzed. This analysis is used to define the retention time windows for the multiple analyte groups.

3.3.2 Qualitative Identification

The patterns within the retention time window for the sample extract are compared to the pattern within the same window of the reference oil solution. The magnitude of the individual peaks may not be consistent but the location of the peaks within the window should be similar between the two analyses.

3.4 Calibration Criteria

3.4.1 Initial Calibration

A five-point calibration curve based on response factors is established to demonstrate the linearity of the detector. The recommended standard concentrations are approximately 20, 100, 250, 500, and 1000 ng/mL (Table 4).

3.4.1.1 The QC acceptance criteria for linearity of the initial calibration curve requires that the percent relative standard deviation (RSD) of the response factors for each compound in the five calibration standards must be less than or equal to fifteen percent ($\leq$ 15%). If these RSD criteria are exceeded, the linearity of the initial calibration curve can be determined to be acceptable if the correlation coefficient (r) determined using linear least squares regression analyses is greater than or equal to 0.99. The instrument software generates and prints out both types of calibration data for all initial calibration determinations, which are maintained in calibration files with the raw data for that laboratory area.

3.4.2 Continuing Calibration Verification (CCV)

Calibration verification must be performed at the beginning of each analytical sequence. A calibration verification is also required at the end of a 12 hour shift or at the end of the analytical sequence, whichever is more frequent.

3.4.2.1 QC acceptance criteria are based upon daily response factors for each compound which are compared to the mean response factors for the initial calibration curve. If the average daily response factors for all analytes is within ±15% of the calibration value, analyses may proceed. If, for any single analyte, the daily response factor exceeds ±25 percent of calibration value, the five-point calibration is repeated before analysis continues and all samples are re-analyzed back to last passing CCV.

3.4.3 GERG Standard Check

The GERG Standard Check Solution is analyzed with all analytical batches. The laboratory certified concentration range of compounds in the standard check solution has been defined as the average concentration of all previous analyses plus or minus one standard deviation.

The QC acceptance criteria for the measured concentration of the standard check compounds must be within ±25% of the laboratory certified concentration on average for all analytes greater than the LCL and not exceed 35% for any individual analyte. If, after re-analysis, the concentration for any single target compounds exceeds ±35% of the calibration value, corrective action such as instrument maintenance or a new five point calibration must be prepared prior to further analysis.

3.5 Criteria for QC Samples in an Analytical Batch

The acceptance criteria for QC samples are evaluated within an analytical group. Therefore, failure of one QC sample type does not necessarily cause the entire analytical batch to fail.

3.5.1 Method Blank (BLANK)

3.5.1.1 A Method Blank is used to demonstrate freedom from contamination in the analytical procedure, and is required for each set of 20 or fewer samples.

3.5.1.2 If any of the target compounds are found in the blank at greater than 3 x the MDL, re-extraction of the entire set may be required as specified in the following subsections.

3.5.1.2.1 If any of the target compounds are found in the blank at greater than 3 x the MDL, but are not detected in the analytical samples above the MDL, the analytical data can be reported and must be flagged, but no further action is required.

3.5.1.2.2 When target compounds are present in the method blank and in the analytical samples at concentrations above 3 x the MDL and the concentration in a sample is 10 x that found in the blank, the blank must be flagged but sample data are reportable and are not flagged.

3.5.1.2.3 When target compounds are present in the method blank and in the analytical samples at concentrations above 3 x the MDL and the concentration in the sample is less than 10 x that found in the blank, the sample should be re-extracted and re-analyzed. If

no sample remains for re-extraction, the analytical data for those analytes in the blank and samples can be reported but must be flagged.

3.5.2 Laboratory Blank Spike (LBS) and Laboratory Blank Spike Duplicate (LBSD)

3.5.2.1 A Laboratory Blank Spike (LBS) may be used to estimate analytical accuracy of the method if inadequate sample is available or if a complex matrix is present . It may be required with each set of 20 or fewer samples.

3.5.2.2 A Laboratory Blank Spike Duplicate (LBSD) is used to estimate both analytical accuracy and precision and may be required for each set of 20 or fewer samples.

3.5.2.3 QC acceptance criteria for the target compound recoveries are that the recovery for each target compound falls between 40 and 120%.

3.5.2.4 If the LBSD has been included, the recoveries determined from the LBS and LBSD should agree within an average Relative Percent Difference (RPD) of $\leq$25%.

3.5.2.5 If two or more of the target compounds are outside the QC acceptance criteria corrective action may be indicated. Corrective action may include recalculation and/or reanalysis of the LBS and LBSD; re-extraction of the sample group; or instrument maintenance and/or recalibration. A laboratory blank spike may be used to demonstrate that the analytical system is in control when working with a difficult matrix or sample set.

3.5.3 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)

3.5.3.1 A Matrix Spike (MS) sample is used to estimate analytical accuracy in the presence of a representative matrix and is normally required for each set of 20 or fewer samples.

3.5.3.2 A Matrix Spike Duplicate (MSD) is used to estimate analytical accuracy and precision in the presence of a representative matrix and may be required for each set of 20 or fewer samples.

3.5.3.3 QC acceptance criteria for target compound recoveries in the MS and the MSD is 40 to 120% of the spiked amount. In computing the QC acceptance criteria, only valid spikes will be used. In a valid spike, the amount of analyte added is at least as much as was originally present in the sample.

3.5.3.4 If a Matrix Spike Duplicate (MSD) has been included with the analytical batch, the recoveries determined from the MS and MSD samples should agree within a Relative Percent Difference (RPD) of $\leq$25%.

3.5.3.5 The MS and MSD acceptance criteria are advisory. However, if two or more of the target compounds are outside the QC acceptance criteria corrective action may be indicated. Corrective action may include recalculation and/or reanalysis of the MS and MSD; re-extraction of the sample/MS/MSD group; or instrument maintenance and/or recalibration.

3.5.4 Duplicate (DUP)

3.5.4.1 A sample Duplicate (DUP) is used to demonstrate sample homogeneity and analytical precision in the presence of a representative matrix and may be required with each set of 20 or fewer samples.

3.5.4.2 QC acceptance criteria for analyte concentrations greater than ten times the MDL is a Relative Percent Difference (RPD) of $\leq$25%.

3.5.4.3 If the RPD is outside the QC acceptance criteria, corrective action may be indicated. Corrective action may include: recalculation or reanalysis of the DUP and the original sample, instrument maintenance, recalibration, or re-extraction of the analytical batch.

3.5.5 Standard Reference Material (SRM)

3.5.5.1 A Standard Reference Material (SRM) is used to demonstrate analytical accuracy and may be required with each set of 20 or fewer samples.

3.5.5.2 When requested, a standard reference material is extracted and analyzed with each batch of samples. Acceptable concentrations are defined as the range of the documented (certified or reference) concentration plus or minus the 95% confidence limits in the certification.

3.5.5.3 The QC acceptance criteria are that 80% of the data for measured concentrations should be within ±30% of the range of the acceptable concentration for each target compound (either certified or non-certified) with concentrations greater than 10 times the MDL. Corrective action may include recalibration or re-analysis of the SRM, instrument maintenance, re-calibration, or re-extraction of the analytical batch.

3.5.6 Surrogate Compound Recovery

3.5.6.1 All samples are spiked with the appropriate surrogate spiking solution to determine the concentration of

target compounds and to monitor method performance.

3.4.6.2 QC acceptance criteria for surrogate compound recovery is 40 to 120% for all except d12-perylene. The recovery of this surrogate is advisory only.

3.5.6.3 If surrogate recovery fails the QC acceptance criteria, the following corrective action will be taken:

a. The calculations are checked to ensure that there are no errors.

b. The internal standard and surrogate solutions are checked for degradation, contamination, etc., and the instrument performance is checked.

c. If the surrogate recovery is outside the control limits, the secondary ion may be used to check the quantitation of the surrogate. If the secondary ion is within the control limits, this recovery can be used and the data are appropriately annotated.

d. If the upper control limit is exceeded for only one surrogate, and the instrument calibration and other surrogate standard concentrations are in control, it is concluded that an interference specific to the surrogate was present that resulted in high recovery and that this interference does not affect the quantitation of other target compounds. The presence of this type of interference is confirmed by evaluation of chromatographic peak shapes. To correct for the underestimation of the analyte concentration based on this surrogate, the target compounds will be quantified using the surrogate that is chromatographically closest to the surrogate exhibiting interference.

e. If the surrogate cannot be measured because the amount and nature of interferants in the sample, the target compounds based on that surrogate will be quantified based on the closest surrogate. The surrogate recovery is appropriately qualified.

f. If the native concentration of hydrocarbons are high and require dilution for acceptable chromatographic separations, a dilution is made. A known aliquot of the extract is removed. One hundred (100) µL of surrogate are added and the volume brought to 1.0 mL. The appropriate changes are made in the dilution factor within the quantitation software and the sample is re-analyzed. There is no concentration correction based on the surrogate recovery for dilution results. The surrogate recoveries are not reported but qualified with a "D" to denote the dilution. The MDL must also be adjusted to account for any dilutions.

g. The extract is reanalyzed if the steps above fail to reveal a problem. If reanalysis of the extract yields surrogate recoveries within the stated limits, then the reanalysis data is reported. If reanalysis does not yield acceptable recoveries, the samples will be re-extracted. If re-analysis does not improve surrogate recovery, the data are reported and properly qualified.

4.0 APPARATUS AND MATERIALS

4.1 Gas Chromatograph/Mass Spectrometer

Representative aliquots are injected into the capillary column of the gas chromatograph using the following conditions:

Injector Temp: 300°C
Transfer Line Temp: 280°C

Initial Oven Temp:	60°C
Initial Hold Time:	0 min.
Ramp Rate:	12°C
Final Temperature:	300°C
Final Hold Time:	18 min.

The effluent from the GC capillary column is routed directly into the ion source of the mass spectrometer. The MS is operated in the selected ion monitoring (SIM) mode using appropriate windows to include the quantitation and confirmation masses for the PAHs listed in Table 3. For all compounds detected at a concentration above the MDL the confirmation ion is checked to confirm its presence.

The analytical system includes a temperature programmable gas chromatograph (Hewlett-Packard 5890A, or equivalent). The injection port is designed for split or splitless injection and analyses are conducted in the splitless mode. A 30-m long x 0.32-mm I.D. fused silica capillary column with DB-5MS bonded phase (J&W Scientific) is used. The autosampler is capable of making 1 to 4 µL injections.

The mass spectrometer (HP 5970/72 MSD) operates at 70 eV electron energy in the electron impact ionization mode and is tuned to maximize the sensitivity of the instrument based on manufacturer specifications.

5.0 ANALYTICAL STANDARDS

5.1 Surrogate Spiking Solution

A surrogate solution is made by weighing appropriate amounts of pure compounds into a volumetric flask and diluting to volume with methylene chloride (or by purchase of a certified standard (NIST) or equivalent). Surrogates are added to the samples prior to extraction at a concentration of approximately 10 x the MDL. If higher concentrations of hydrocarbons are anticipated, the surrogate concentration can be appropriately increased.

The compounds in the surrogate solution are deuterated aromatics (Table 1). The concentration of the surrogate solution requires the addition of 100 µL to the extract, leading to a surrogate final concentration of 40 ng/mL in the final extract volume. All sample target compound concentrations are corrected for surrogate recoveries.

5.2 Internal Standard Solutions

A solution containing two internal standards at 20 µg/mL is prepared based on weight from a certified standard (NIST or equivalent). The stock solution is transferred to a volumetric flask and diluted to volume with methylene chloride. The internal standards are deuterated aromatics (Table 1). Sufficient internal standard solution is added to the extract just prior to instrumental analysis to give a final concentration of 40 ng/mL in the final extract volume.

5.3 Spiking Solution

A solution containing selected PAHs is used to fortify blank spikes and matrix spike samples. A certified solution is purchased from a commercial vendor and diluted with methylene chloride to the appropriate working concentration. Dibenzothiophene is weighed neat and added to the spiking solution to make a final concentration of about 1.0 µg/mL. The spiking solution is added to give a final concentration of approximately 10 x the MDL. If higher concentrations of hydrocarbons are anticipated, the matrix spike can be appropriately increased.

5.4 GERG Standard Check Solution

A solution of a laboratory reference oil is analyzed as an instrument standard check solution with each analytical batch. The concentration of oil is approximately 0.8 mg/mL. The oil is weighed into a volumetric flask and brought to volume with methylene chloride.

6.0 INSTRUMENT CALIBRATION PROCEDURE

6.1 Initial Calibration

Initial calibration is required before any sample is analyzed for PAHs. Initial calibration is also required if the analysis of a calibration verification standard does not meet the required criteria listed in Section 3.1.1.

6.1.1 Tune the instrument with PFTBA as described in Section 3.1.1.

6.1.2 Using the same GC and MS conditions that produced acceptable tune results, analyze a 2 µL portion of each of the five calibration

solutions once, and demonstrate that the following conditions are met.

6.1.2.1 The ratio of integrated ion currents for the quantitation and confirmation ions appearing in Table 3 must be within ±30% the indicated percent relative abundance established for each compound.

6.1.2.2 The ratio of integrated ion currents for the quantification and confirmation ions belonging to the surrogates and the internal standards must be within the ±30% of the relative abundance stipulated in Table 3.

Note: All ratios must be within the specified acceptance limits simultaneously in one run. Otherwise, corrective action is necessary.

6.1.4 For each injection, calculate the relative response factors (RRF) for target compounds relative to their appropriate quantitation standards according to Equation 1.

The following formula is used to calculate the response factors (RRF) of target compounds relative to its reference surrogate in the calibration standards.

Equation 1. $RRF = (A_s C_{su})/(A_{su} C_s)$

where:

A_s = Area of the quantitation ion for the target compound.
A_{su} = Area of the quantitation ion for the surrogate.
C_{su} = Concentration of the surrogate (ng/µL).
C_s = Concentration of the target compound to be measured (ng/µL).

Note: The response factors for the multi-analyte groups are assumed to be that of the parent compound.

6.1.5 Calculate the mean response factors ($\overline{RRF}$ s) for the five calibration solutions using Equation 2.

Equation 2. $$\overline{RRF} = \left(\frac{1}{5}\right) \sum_{j=1}^{5} RRF_j$$

where:

j = the injection number or calibration solution number (j = 1 to 5).

6.1.6 Determine the respective percent relative standard deviation for each compound in the calibration standards (%RSD) by dividing the standard deviation by the mean response factor and multiplying the result by 100. Document that the initial calibration meets all of the acceptance criteria outlined in Section 3.4.1.

6.2 Continuing Calibration Verification

Continuing calibration verification must be performed at the beginning of an analytical sequence following successful MS tune except when following an initial calibration. A continuing calibration verification is also required at the end of a 12 hour analysis period or at the end of the analytical sequence, whichever is more frequent.

6.2.1 Using the same GC and MS conditions that were used for the initial calibration, analyze a 2 µL portion of the 250 ng/mL calibration solution and evaluate it with the following QC acceptance criteria.

6.2.1.1 The ratio of integrated ion currents for the quantitation and confirmation ions appearing in Table 3 must be within the ±30% of the relative abundance established for each target compound.

6.2.1.2 The ratio of integrated ion currents of the quantitation and confirmation ions for the surrogate and internal standards

must be within the ±30% of the relative abundance stipulated in Table 3.

NOTE: All ratios must be within the specified acceptance limits simultaneously in one run. Otherwise, corrective action is necessary.

6.2.2 Calculate the daily response factor for the target compounds using Equation 1.

6.2.3 These daily response factors for each compound are then compared to the mean response factors from the initial calibration curve. The percent difference is calculated using the following equation:

$$\text{Percent Difference} = \frac{(\overline{RRF} - RFC) \times 100}{\overline{RRF}}$$

where:

$\overline{RRF}$ = Mean response factor from initial calibration.

RFC = Response factor from current verification check standard.

The QC acceptance criteria requires that the average daily response factors for all analytes must be within ±15% of the calibration value for the analyses to proceed. If, for any single analyte, the daily response factor exceeds ±25 percent of the calibration value, the five point calibration must be repeated prior to further analysis.

7.0 REQUIRED SAMPLE DOCUMENTATION AND IDENTIFICATION

Copies of the following documents, if applicable, must accompany the sample set in a labeled folder when it is delivered to GC/MS analysis group:

Chain-of-custody documents
Sample Information Sheet(s)
Analysis Request Form(s)
Laboratory bench sheet
Dry weight bench sheet
Percent lipid bench sheet for tissue samples
Sample Action Request Form(s)

8.0 SAMPLE ANALYSIS

8.1 Tune the instrument with PFTBA as described in Section 3.1.1.

8.2 Inject 2 µL of methylene chloride as an instrument blank, and acquire SIM mass spectra data as described in Section 4.1. Demonstrate and document that the analytical system is free from interfering contamination.

8.3 Inject 2 µL of the GERG Standard Check Solution and acquire SIM mass spectral data as described in Section 4.1. Demonstrate and document that the retention time windows have been established (Section 3.3) and the criteria listed in Section 3.4.3 are met.

8.4 Inject 2 µL of the calibration verification standard (250 ng/mL) and acquire SIM mass spectral data as described in Section 4.1. Demonstrate and document that the criteria listed in Section 3.4.2.1 are met.

8.5 Inject 2 µL of the sample extract and acquire SIM mass spectral data under the same conditions that have been established to produce acceptable results.

8.6 Qualitative Identification

For a gas chromatographic peak to be identified as a target compound, it must meet all of the criteria specified in Section 3.2 for single analyte compounds and Section 3.3 for multiple analyte compounds.

8.7 Quantitative Determination

8.7.1 For gas chromatographic peaks that have met all the qualitative identification criteria, calculate the concentration of the target compounds using Equation 3.

Based on these response factors, sample extract concentrations for each analyte is calculated using the following formula:

Equation 3. $$C = \frac{(A_S)(C_{SU})}{(A_{SU})(\overline{RRF})(Sa)}$$

where:

C	=	Concentration in sample (ng/gram or ng/liter).
Sa	=	Sample amount (grams, liters).
A_S	=	Area of the quantitation ion for the target compound to be measured.
A_{SU}	=	Area of the quantitation ion for the surrogate.
C_{SU}	=	Amount of surrogate added to each extract (ng).
$\overline{RRF}$	=	Average response factor

8.7.2 Calculate the percent recovery of the five surrogate quantitation standards in the sample extract using Equation 4.

Equation 4. $$\%\ \text{recovery} = \frac{(A_{SU} \times C_{IS})}{(C_{SU} \times A_{IS} \times \overline{RRF}_{SU})}$$

where:

A_{IS}	=	Area of the quantitation ion for the appropriate internal standard
A_{SU}	=	Area of the quantitation ion for the surrogate
C_{SU}	=	ng of deuterated surrogate added to the sample
C_{IS}	=	ng of deuterated internal standard added to the sample extract

$\overline{RRF}_{SU}$ = Average response factor for the surrogate based on the internal standard from the initial calibration.

The laboratory will take corrective action whenever the recovery of any surrogates is less than 40% or greater than 120%.

8.7.3 If the concentration in the final extract of any of the target compounds exceeds the upper method calibration limit, the sample extract must be diluted by an appropriate dilution factor and reanalyzed. Detection limits must also be adjusted to compensate for sample dilution.

8.7.4 Calculate and report the Relative Percent Difference (RPD) between duplicate sample results.

8.7.5 Calculate and report the % Recovery of target compounds in the Matrix Spike (MS), Matrix Spike Duplicate (MSD), and, if analyzed, in the Laboratory Blank Spike (LBS) samples.

9.0 INSTRUMENT MAINTENANCE

9.1 Gas Chromatograph Maintenance

9.1.1 The syringe is cleaned by rinsing with appropriate solvent after each injection.

9.1.2 A new injection port liner and septum are installed at the beginning of each new run sequence.

9.1.3 A new injection port base plate is installed as needed.

9.1.4 One to two feet of the analytical column are removed as needed. This is necessary when there is significant tailing of the peak shapes.

9.1.5 The tank of carrier gas (He) is replaced when the pressure falls below 500 psi.

9.1.6 All instrument maintenance is recorded in the maintenance log for the specific instrument.

9.2 Mass Spectrometer Maintenance

9.2.1 The emission filament is replaced as necessary.

9.2.2 The source assembly is cleaned and replaced as necessary.

9.2.3 The PFTBA reservoir is refilled as necessary.

9.2.4 The transfer line/re-entrant assembly is disassembled, cleaned or repaired and reassembled as necessary.

9.2.5 The rotary pump oil is changed yearly, or more frequently if indicated.

9.2.6 The diffusion pump oil is changed as necessary.

9.2.7 All maintenance is recorded in the maintenance log for the specific instrument.

10.0 DOCUMENTATION REQUIRED FOR ANALYTICAL RESULTS

10.1 All injections and analytical run sequences are recorded on a computer printout kept on file at the instrument.

10.2 For all Initial Calibrations the following documentation is printed and maintained for a period of at least one year.

10.2.1 The Selected Ion Current Profile (SICP) for each ion in each calibration run including any manual integrations.

10.2.2 Listing of retention times and peak areas for all target analytes in each calibration run.

10.2.3 Listing of the calculated Relative Response Factors (RRF) for all target compounds in each calibration run.

10.2.4 Listing of the calculated Average Relative Response Factors ($\overline{RRF}$) for all target compounds, the standard deviation and percent relative standard deviation for each $\overline{RRF}$.

10.3 For all Calibration Verifications, the following documentation is printed and maintained for a period at least one year.

10.3.1 The Selected Ion Current Profile (SICP) for each ion in the calibration run including any manual integrations,

10.3.2 Listing of retention times and peak areas for all target compounds in the calibration run, and

10.3.3 Listing of the analyte concentrations for all target compounds in the calibration run.

10.4 For all methylene chloride instrument blanks the following documentation is printed and maintained for a period of at least one year.

10.4.1 The Selected Ion Current Profile (SICP) for each ion in the blank run demonstrating that the analytical system is free from contaminating interferences.

10.5 For all analytical and laboratory Quality Control samples the following documentation is printed and maintained for a period of at least one year (actual retention of analytical data is determined by the contract guidelines, but shall not be less than one year).

10.5.1 The Selected Ion Current Profile (SICP) for each ion in the analytical run, including any manual integrations,

10.5.2 Listing of retention times and peak areas for all target compounds in the analytical run,

10.5.3 Listing of the calculated concentrations of all target compounds, percent recovery of the surrogates, and

10.5.4 A compiled data report in either the GERG standard format or other customized format requested by the client. The compiled data report includes Relative Percent Difference (RPD) between duplicate analyses or MS/MSD recoveries, and percent recovery of native analytes in LBS and MS/MSD QC samples.

Table 1. Polynuclear Aromatic Hydrocarbons of Interest.

Compounds	I.S. Reference	Surrogate Reference	Compounds	I.S. Reference	Reference Surrogate
Naphthalene	A	1	Fluoranthene	B	3
C_1-Naphthalenes	A	1	C_1-Fluoranthenes[a]	B	3
C_2-Naphthalenes	A	2			
C_3-Naphthalenes	A	2	Pyrene	B	3
C_4-Naphthalenes[a]	A	2	C_1-Pyrene	B	3
Biphenyl	A	2	Benzo[a]anthracene	B	4
Acenaphthylene	A	2			
			Chrysene	B	4
Acenaphthene	A	2	C_1-Chrysene[a]	B	4
			C_2-Chrysene[a]	B	4
Fluorene	A	2	C_3-Chrysene[a]	B	4
C_1-Fluorenes[a]	A	2	C_4-Chrysene[a]	B	4
C_2-Fluorenes[a]	A	2			
C_3-Fluorenes[a]	A	2	[Benzo[b]fluoranthene, Benzo[k]fluoranthene]-sum	B	4
Dibenzothiophene	A	3	Benzo[e]pyrene	B	4
C_1-Dibenzothiophenes[a]	A	3	Benzo[a]pyrene	B	4
C_2-Dibenzothiophenes[a]	A	3	Perylene	B	5
C_3-Dibenzothiophenes[a]	A	3	Indeno[1,2,3-c,d]pyrene	B	4
			Dibenzo[a,h]anthracene	B	4
Phenanthrene	A	3	Benzo[g,h,i]perylene	B	4
C_1-Phenanthrenes	A	3			
C_2-Phenanthrenes[a]	A	3	Specific Isomers		
C_3-Phenanthrenes[a]	A	3			
C_4-Phenanthrenes[a]	A	3	1-methylnaphthalene	B	1
			2-methylnaphthalene	B	1
Anthracene	A	3	2,6-dimethylnaphthalene	B	2
C_1-Anthracenes[a]	A	3	2,3,5-trimethylnapthalene	B	2
C_2-Anthracenes[a]	A	3	1-methylphenanthrene	B	3
C_3-Anthracenes[a]	A	3			
C_4-Anthracenes[a]	A	3	Surrogates		
Internal Standards			Naphthalene-d_8	(1)	
			Acenaphthene-d_{10}	(2)	
Fluorene-d_{10}	(A)		Phenanthrene-d_{10}	(3)	
Benzo (a) pyrene-d_{12}	(B)		Chrysene-d_{12}	(4)	
			Perylene-d_{12}	(5)	

[a]Alkylated homologues not included in the calibration solution.

NOTE: Alkylated phenanthrenes and anthracenes, and alkylated fluoranthenes and pyrenes are quantified together as total alkylated (Cx) phenanthrene/anthracenes and total alkylated (Cx) fluoranthenes/pyrenes. Only the parent compounds and specific isomers are reported as individual compounds.

Table 2. Summary of QC Requirements for Quantitative Analysis

Element	Control Limit Criteria	Frequency
- Instrument Calibration	Minimum of 5 standards; correlation coefficient of $\geq$ 0.99 or % RSD within ± 15% for all target compounds.	Initial and after any failures of continuing calibrations.
- Instrument Blank	Instrument free of interfering contamination or perform necessary maintenance.	Prior to analysis of all analytical batches.
- GERG Standard Check	Analytes within ± 25% or average of lab certified concentration with no analytes > 35% or recalibrate.	Prior to analysis of all analytical batches.
- Continuing Calibration Verification (CCV)	Percent difference for all response factors within ± 15% or average of initial calibration; no single analyte greater than 25% or recalibrate and reanalyze back to last passing CCV.	After daily MS tune; once every 12 hours during the analytical sequence and at end of analytical sequence.
- Surrogate Recovery	Recovery of 40 to 120% for all surrogates. See Section 3.5.6 for corrective actions.	All samples.
- Method Blank	No analytes > 3x MDL. See Section 3.5.1 for exceptions to need for re-extraction.	One per QC batch.
- Duplicates (if applicable)	RPD $\leq$ 25% for all analytes > 10 x MDL. See Section 3.5.4 for corrective action.	One per QC batch.
- Matrix Spike, Matrix Spike Duplicate (if applicable)	% recovery within 40 to 120%. RPD for the spike recoveries should be $\leq$ 25% for all analytes. See Sections 3.5.3 for corrective actions.	One per QC batch.
- Standard Reference Material (if applicable)	Recovery of 80% of certified or non-certified compounds within 30% of certified range for those analytes > 10x MDL. See Section 3.5.5 for corrective action.	One per QC batch.

Table 3. Parameters for Target Analytes.

Compound	Quant. Ion	Conf. Ions	% Rel. Abund. of Conf. Ions
d_8-Naphthalene	136	134	15
Naphthalene	128	127	15
C_1-Naphthalenes (including isomers)	142	141	80
C_2-Naphthalenes	156	141	NA
C_3-Naphthalenes	170	155	NA
C_4-Naphthalenes	184	169,141	NA
d_{10}-Acenaphthene	164	162	95
Acenaphthylene	152	153	15
Biphenyl	154	152	30
Acenaphthene	154	153	98
d_{10}-Fluorene	176	174	85
Fluorene	166	165	95
C_1Fluorenes	180	165	NA
C_2-Fluorenes	194	179	NA
C_3-Fluorenes	208	193	NA
d_{10}-Phenanthrene	188	184	15
Phenanthrene	178	176	20
Anthracene	178	176	20
C_1-Phenanthrenes/anthracenes	192	191	NA
C_2-Phenanthrenes/anthracenes	206	191	NA
C_3-Phenanthrenes/anthracenes	220	205	NA
C_4-Phenanthrenes/anthracenes	234	219,191	NA
Dibenzothiophene	184	152,139	15
C_1-Dibenzothiophenes	198	184,197	NA
C_2-Dibenzothiophenes	212	197	NA
C_3-Dibenzothiophenes	226	211	NA
Fluoranthene	202	101	15
d_{12}-Chrysene	240	236	30
Pyrene	202	101	15
C_1-Fluoranthenes/pyrenes	216	215	NA
Benzo [a] anthracene	228	226	20

NA = Not Applicable

Table 3. (Cont.)

Compound	Quant. Ion	Conf. Ions	% Rel. Abund. of Conf. Ions
Chrysene	228	226	30
C_1-Chrysenes	242	241	NA
C_2-Chrysenes	256	241	NA
C_3-Chrysenes	270	255	NA
C_4-Chrysenes	284	269,241	NA
d_{12}-Benz (a)pyrene	264	260	20
Benzo [b] fluoranthene	252	253,125	30, 10
Benzo [k] fluoranthene	252	253, 125	30, 10
Benzo (e) pyrene	252	253	30
Perylene	252	253	20
d_{12}-Perylene	264	260	22
Benzo [a] pyrene	252	253, 125	30, 10
Indeno[1,2,3-c,d]pyrene	276	277, 138	25,30
Dibenzo [a,h] anthracene	278	279, 139	25,20
Benzo [g,h,i]perylene	276	277, 138	25,20

NA = Not Applicable

Table 4. PAH Matrix Spike Compounds in CH_2Cl_2.

Compound	Spiking Solution Concentration (µg/mL)
Naphthalene	1.030 ± 0.10
1-Methylnaphthalene	1.24 ± 0.5
2-Methylnaphthalene	1.18 ± 0.04
Biphenyl	1.046 ± 0.04
2,6-Dimethylnaphthalene	1.08 ± 0.4
Acenaphthylene	1.040 ± 0.07
Acenaphthene	1.089 ± 0.15
2,3,5-Trimethylnaphthalene	0.99 ± 0.4
Fluorene	1.087 ± 0.08
Dibenzothiophene	~1.000
Phenanthrene	1.048 ± 0.07
Anthracene	1.169 ± 0.06
1-Methylphenanthrene	1.04 ± 0.3
Fluoranthene	0.884 ± 0.06
Pyrene	0.881 ± 0.08
Benz[a]anthracene	7.85 ± 0.05
Chrysene	1.050 ± 0.06
Benzo[b]fluoranthene	0.785 ± 0.05
Benzo[k]fluoranthene	0.833 ± 0.12
Benzo[e]pyrene	0.840 ± 0.04
Benzo[a]pyrene	1.014 ± 0.09
Perylene	1.065 ± 0.06
Indeno[1,2,3-cd]pyrene	0.940 ± 0.07
Dibenz[a,h]anthracene	0.774 ± 0.18
Benzo[ghi]perylene	0.790 ± 0.13